Geo Environmental Assessment on Abandoned Mine Filling with Coal Ash

A Thesis Submitted in Partial Fulfillment of the Requirements for the

Degree of

Master of Technology

In

Civil Engineering

SOUMYAPRAKASH SAHOO

DEPARTMENT OF CIVIL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

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Under the guidance and supervision of

Prof C.R.Patra

Submitted By

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2014

Dedicated

To

Mr Pramod Kumar Sahoo

&

Mrs Sanjikta Sahoo

NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA

CERTIFICATE

This is to certify that the thesis entitled "***Geo Environmental Assessment Of Abandoned Mine Filling With Coal Ash***" being submitted by Soumyaprakash Sahoo is partial fulfilment of the requirements for the award of **Master Of Technology** in **Civil Engineering** with specialization in **GEOTECHNICAL ENGINEERING** at National Institute Of Technology Rourkela, is an authentic work carried out by his under my guidance and supervision.

To the best of my knowledge, the matter embodied in this report has not been submitted to any other university/institute for the award of any degree or diploma.

Place: Rourkela

Date:

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Soumyaprakash Sahoo

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Abstract

In India, large quantity of fly ash is produced from coal based thermal power plants because most of our energy demand is fulfilled through coal based resources. In our country fly ash generation increased from 40 million tons to 135 million tons in between 1994 to 2012. As per Technology Information Forecasting and Assessment Council and Fly Ash Utilization Programme, the generation of ash is expected in between 300-400 MT in 2017, 500MT in 2022 and 1000 MT/YR in 2032. In the future, production rate of fly ash is likely to increase drastically to meet power demand for number of coal based power plants contributing to total power production is around 80%. Indian coals are generally low in sulphur content, due to which, huge amount of ash is generated during its burning. Also disposal of these ashes in land without proper disposal facilities causes environmental pollution. A number of researchers have discussed the utilization of coal ash in various Geotechnical applications.

For minimizing surface subsidence, river sand is mostly used in abandoned coal mines filling. Due to increase in the use of the river sand in the construction industries, the mining industries are facing scarcity of river sand to fill abandoned mine. After extraction of coal from mines, large number of coal mines leave without filling, which creates surface subsidence. Therefore, the mining industry is searching for an alternate filling material which is easily available in large quantity and in minimal cost. The present work aims to characterize and utilize the largely available coal ashes in abandoned mine filling applications and to study the various issues related to geo- environmental aspects of the same.

From the experimental results, it is concluded that coal ashes can replace the conventional river sand normally used for mine filling applications and thereby cost of the project as well as the environmental problems relating to coal ash can be reduced to a significant extent. It was observed that the water holding capacity of bottom ash considerably

lower than pond and fly ashes. XRD results show that coal ash has more numbers of quartz, mullite and iron oxide peaks. The coal ash used in this study is classified under Class ‘F’ according to ASTM C618. However, in general Class ‘F’ fly ash can provide a better filler material than Class ‘C’ fly ash, because the calcium content is low. Heavy metal concentrations were leached more from fly ash as compared to bottom ash and pond ash. Initially, when neutral coal ash is mixed with acidic water, the pH value increases and after 24 hours it gradually decreases and attains value confirming to drinking water standard.

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CHAPTER-1

INTRODUCTION

In India, large quantity of fly ash is produced from coal based thermal power plants because most of our energy demand is fulfilled through coal based resources. In our country fly ash generation increased from 40 Million Tons to 135 Million Tons in between 1994 to 2012. As per Technology Information Forecasting and Assessment Council (TIFAC) and Fly Ash Utilization Programme (FAUP), the generation of ash is 300-400 MT in 2017, 500MT in 2022 and 1000 MT/YR in 2032. In the future, production rate of fly ash is likely to increase drastically to meet power demand for number of coal based power plants contributing around 80% of total power production. However, current utilization of fly ash is rather limited and also safe removal of this huge amount of fly ash is a big deal in order to mitigate environmental issues arising from current disposal method. Coal is plenty available, has been a main cause of energy till date and is likely to remain so in near future. Indian coals are low in sulphur which generate huge amount of ash (about 35-45%), which leads to huge generation of fly ash in India. Due to disposal of coal ash in the land causes environmental pollution due to leaching of its toxic metal. The utilization of coal ashes is limited for geotechnical purposes. However, many researchers discussed the utilization of coal ash in many geotechnical applications. Non-availability and high cost of natural material such as river sand as a filling material in abandoned mines creates problems with mine filling operations and is largely depends on such material. Hence a suitable alternative material has to introduce for the above stated problem and the alternatives proposed should not create any problem with environments. As such, the present investigation is to study the suitability of coal ash in mine filling applications. Hence utilization of a large quantity of coal ash for mine filling and problem related to the environment can be avoided. The present work is also

intended to study the various environmental related issues in the application of coal ashes in such areas through laboratory experiments.

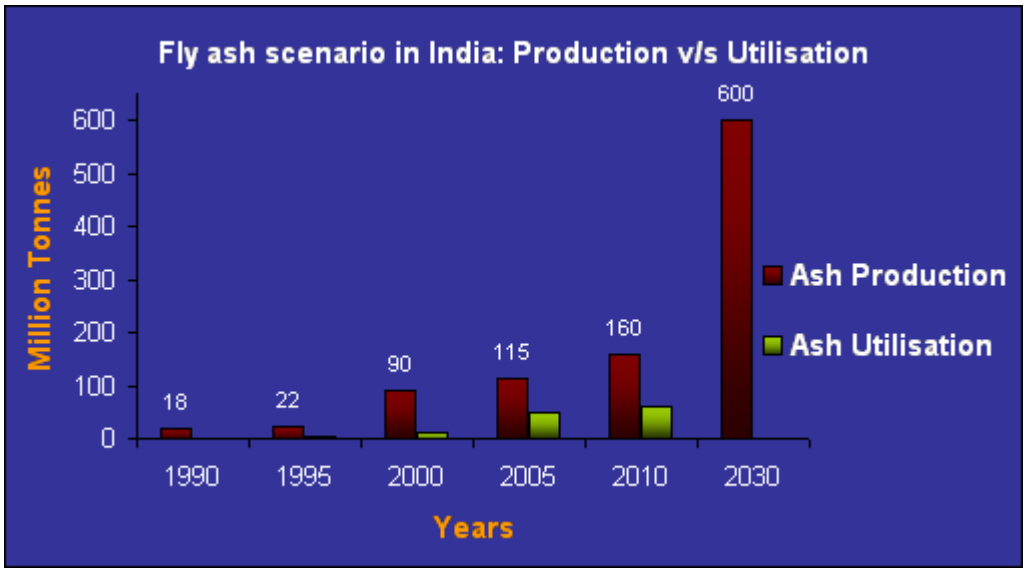

Figure 1.1 Fly ash generation and utilisation by NTPC power plants

(http://cbrienvis.nic.in)

1.1 Origin of Project

Coal is being used effectively in many small scale and large scale thermal power projects in India as it is cost effective and available in large quantity. Coal ash, which is the by-product of combustion of coal in thermal power plants. The largest amount of coal ash (275 Million Tons) is being generated in India in each year and is stored in ash pond as pond ash. Now for storage of pond ash in ash pond occupies nearly 70000 acres of land in each year, which creates problem related to land and environment. In India, utilization of coal ashes in areas like cement manufacturing as a partial replacement of fly ash with cement, manufacturing of cost effective fly ash bricks, base material in road construction, construction of dams and dykes etc. is in practice.

For minimizing surface subsidence, river sand is mostly used in abandoned coal mines filling. Due to increase use of the river sand in civil engineering structures, the mining industry facing shortage of river sand in the abandoned mine filling. Therefore, after

extraction of coal from mines, large numbers of coal mines leave without filling, which creates surface subsidence. Therefore, the mining industry is searching for a substitute filling material which is easily available in large quantity and in minimal cost. Therefore the current research work is to characterize and utilize the largely available coal ashes in abandoned mine filling applications and study the various issues related to geo environmental aspects.

1.2 Objective

The objective of the present study is

- To characterize coal ash collected from TSTPS, Kaniha, Odisha.
- To study leachate characteristics of coal ash by batch leaching and TCLP method.
- To analyse quality of water samples collected near my area in accordance with Indian standard (IS: 10500-2012)
- To study the suitability of coal ash slurry for mine filling application.

CHAPTER-2

LITERATURE REVIEW

2.1 Introduction

Coal ash is the by-product produced largely from coal based thermal power plants in the combustion process (In fig-2.1). Generally, coal ash consists of both fly ash and bottom ash. In which fly ash is collected from electrostatic precipitator since fly ash are very fine particle and fly in nature and large particle like bottom ash falls in the bottom hopper of a coal burning furnace.

Fly ash contributing typically around 85-90% of the total ash production and these lighter, light grey powder material are made up of glass spheres whose size varies from sub-micron to 100 microns (98% lesser than 75 microns, 70-80% smaller than 45 microns). In general, fly ash found to have low specific gravity and density. Due to fine in nature, fly ash specific surface area lies between 2000-6800 sq. cm per gram. Also, this ash contains a small portion of hollow spherical particle called cenosphere having a particularly 0.4-0.6 ton per cubic meter of bulk density, which constitute up to 5% of the ash weight. Cenosphere are suitable to utilize for special industrial applications.

Bottom ash constitutes about 10%-15% of the overall ash produced. Bottom ash has a look same to dark grey coarse sand and particles are clusters of micron-sized granules, up to 10 mm diameter (60-70% lesser than 2 mm, 10-20% smaller than 75 microns). Bottom ash has a maximum density and bulk density of 1200-1500 kg per cubic meter and 1 ton per cubic meter respectively.

In India, wet disposal of fly ash is adopted by most of the power plants in which both fly ash and bottom ash are mixed with sufficient amount of water (75 to 80%) to form fly ash slurry which was transported and disposed of in ash pond. After settling of ash particles the free

standing water is discharged to a natural water stream. The so called settled ash is generally referred to as pond ash.

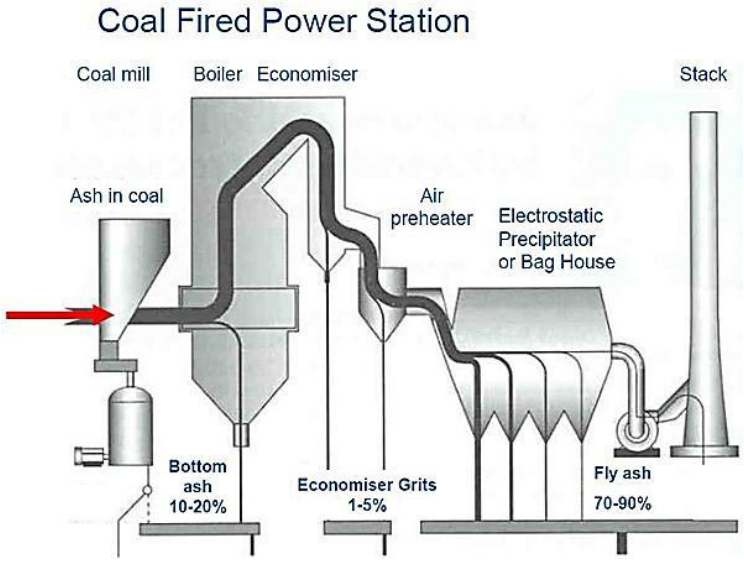

Figure 2.1 Schematic diagram of ash generation in power plant

(http://www.flyashaustralia.com.au)

2.2 Review of Literature

In this section, literature related to leaching of coal ash and some of the case study of mine filling by coal ash has been reported.

Suresh et al. (1998) presented that ash pond is a common available dumping facility for thermal power plants. The pond ash is exposed to weathering and the metals present in ash travel to the soil and consequently to the ground water over a period of time. At Vijayawada thermal power station, Andhra Pradesh, ground water quality examined has been weakening due to the presence of fly ash ions (macro and micro such as Fe, Ca, Mg etc.) which were leached out from the ash up to some extent. The pollution is likely to rise in the case of toxic and other ions with the passage of time.

Hajarnavis (2000) explained the concentrations of heavy metals in the Indian fly ash are given in Table 2.1.

Table 2.1 List of concentrations of heavy metals in the Indian fly ash by Hajarnavis (2000)

Metal	Concentration (mg/kg)
Fe	193-22785
Cd	20
Cr	4.0-74
Cu	5.0-73
Mn	63-722
Zn	71-815
Pb	71-815
Ni	5-300

Cherry et al. (2001) stated that the Ely Creek watershed in Lee County, VA, USA, holds a lot of abandoned mine land ranges with acidic mine waste that defile most of the river and its combining into Stone Creek. Acidic pH estimations ran from 2.73 to 5.2 at a few stations all through the watershed. Residue had high contamination of iron, aluminium, magnesium and manganese, and living space was halfway to non-supporting at 50% of the stations because of sedimentation. Benthic macro-invertebrate overviews at six of 20 stations examined in the watershed transformed no macro-spineless creatures, while eight others had absolute plenitudes of stand out to nine living beings. Four reference stations held > or = 100 organic objects and no less than 13 various taxa. Ten parameters that were specifically impacted by AMD through physical, chemical, biological and toxicological endpoints were adjusted into an Eco-toxicological rating to structure a score of 0-100 focuses for the 20 testing stations, and the bring down the score the more excellent the AMD stress. Twelve of the 15 examining stations affected by AMD accepted an ETR score of 13.75-57.5, which were arranged as extremely focused on and deserving of the most elevated necessity for future natural reclamation exercises in the watershed.

Praharaj et al. (2002) has reported that Fe, Ba, Cu, Mn, S, Pb, V and Zn were in groundwater near to the ash pond in Angul, Orissa. This is because of high leachability of numerous trace elements from fly ash by the infiltrating rainwater.

Roy et al. (2003) carried out a number of experiments found out that mining affects a huge area of the land and affect the quality of surface and underground water. The contaminants and toxic compounds make it unsafe for drinking and industrial usage, disturbing the hydrology of the area. They discovered that the major sources of liquid effluents were: surface run-off, mine water pumped put during drainage operation, spent water from handling plants, dust extractors and dust suppression systems, and leaches/wash-off from waste/tailing dumps.

As per their findings, Acid mine drainage is produced whenever in a mine of any type permeable formations interacts with the water table, aquifer, or perched water body, or where surface water finds its way into a mine were analysed (particularly pyrites) are present in the ore or country rock. Amongst objectionable features of the acid mine drainage are low pH and high levels of sulphates, iron, and total dissolved solids.

These deplete oxygen levels in the water, increase the toxicity by rendering heavy metals soluble, and create corrosion problems. Acid mine drainage can be effectively controlled by preventing its formation at source, by diluting the acid mine drainage to acceptable effluent quality, and by employing standard waste water treatment methods for neutralization and removal of dissolved solids.

In addition to the acid mine drainage, they claim another source of water pollution to be the carry-off the fine solid particles from the surface mining sites and coal preparation plants, especially during rainy seasons, into the streams and watercourses. Sometimes the overburden is dumped along the banks of the streams and watercourses, causing blockage of

free flow and contamination of water. It has also caused a severe damage to the crops irrigated by the river water downstream.

Plant spillage, truck haulage, conveyor transfer points, and rail wagon loading areas, are common sources contributing fines top the surface runoff. Abandoned mine tailings, coal refuse heaps, spoil heaps, and other waste dumps in the mining area contain significant amounts of dissolved minerals, are chronic sources of stream pollution, apart from presenting eyesore sights. Mining is also responsible for changing the hydrology of an area in many ways. Subsidence due to underground mining affects underground water, disruption of surface drainage patterns and resulting contribution to stream pollution. Sometimes it may change the river course and discharge, thereby affecting the agriculture and flora and fauna of the area.

Ugurul (2004) mentioned, in aquatic environment disposal of coal ash is a big concern for environment due to the leaching of metals from coal ash. In both the ash samples which were collected from ESP and ash pond Ca, Na, K, Mn, Fe, S and Pb indicated greatest leachability, though, Cd, Mg, Cu, Cr, Zn and Co demonstrated least leachability. The leachability of substantial metals was low for the examined fly ash. The low metal leaching because of high pH brought about low damage of the leachate. The leached concentration of Mg, Pb and Mn diminished when they were in contact with normal rock samples from below the ash pond. Then again, the components (Na, K, Mg, Pn, Mn, and SO_4) that don't or that weakly connected with the underlying rock sorts will presumably be transported to the ground water.

The metals from coal ash are mixed with ground water by the help of rain water or surface water. This process is called leaching. This caused pollution in ground water. The concentration of this leached metals are more than drinking water.

Pandiana (2004) proposed that fly ash has a low specific gravity, easily draining nature, ease of compaction, insensitive to changes in moisture content, good frictional properties, etc. can be usefully used in the construction of embankments, roads, reclamation of low-lying areas, fill behind retaining structures, etc. It also helps in preserving the valuable top soil required for growing food.

Mishra et al. (2006) explained fly ash composite material (FCM) as an substitute to sand as a paste backfilling material with the adding of lime and gypsum.

Murarka et al. (2006) presented that the use of Coal Ash and their benefits and limitations on environmentally compatible in mining. The summary is given in a tabular form below.

Table 2.2 List of case studies in mine filling by Murarka et al. (2006)

Mine under Investigation	Major Findings
Wyodak Mine	The normal groundwater quality in the Wyodak site compares satisfactorily with the Wyoming department of Environmental Quality livestock use standard. Mean absorptions of all the measured constituents in wells are at or below livestock standards.
Keensburg Mine	The ground water quality at the Keensburg mine does not appear to be impacted by employment of coal ash.
Trapper Mine	Comparison of the historic groundwater absorption data with Colorado standards show little or no sign of groundwater impacts associated with most of the analysed ingredients.
Savage Mine	The ground water quality at Savage mine does not appear to be impacted by placement of coal ash.
Strom Strip Mine	The down-gradient ground water quality is not affected by coal ash placement. No ash has been sited below the water table, because the ground water table is deeper than the mine floor.

Mine under Investigation	Major Findings
Universal Mine	The coal ash leachate defused the acidic pH, improved alkalinity, essentially removed acidity, and considerably decreased manganese, iron, and sulphate concentrations. There were no signs of any other trace metal migration via the mine seep. However, the coal ash leachate did significantly increase boron concentrations in the mine seep water.
Midwestern Abandoned Mine	Alkaline coal ash decrease infiltration and increased the water quality by neutralization.
The Arnold Willis "City" Underground Coal Mine	Groundwater monitoring records specified that trace metals and sulphides remained natural by the placement of FSS (mixture of FGD scrubber sludge, fly ash, lime, and water).
Harwick Mine Complex	The water quality figures from samples of the mine water indicate no adversarial effect on the water in the Harwick Mine complex.
Clinton County	The addition of grout caused a short-term increase in pH from about 2.3 to about 9, as the alkaline FBC ash neutralized the acidic AMD waters. But within a short period, the pH again became acidic.
Big Gorilla Pit	The Big Gorilla water has continued a consistently high pH value in reply to the placement of ash. One long-term effect of ash placement in the former Big Gorilla mine pool will be the prevention of acidic water invention through the surface mine pool.
Red Oak Mine	The alkalinity from the Coal ash counterbalanced the acidity in mine pool waters, leading to a rise in pH, which in turn caused the precipitation of metals as hydroxides and carbonates within the mine, thereby improving water quality.

Mine under Investigation	Major Findings
Frazee Mine	The coal Ash grout combination can be usefully used for an abandoned underground coal mine to decrease acid formation as well to fill mine voids with a high-strength, low-permeability material that would control mine subsidence. The use of the CCP grout appears to have not caused an undesirable water quality impact either.

Prasad et al. (2007) investigated the ground water feature at the Damoda abandoned open cast mine. They found that fluoride concentrations were initially, significantly higher than the given drinking water specifications, but after that its concentration slowly decreased. Concentrations of manganese were found to be raised above prescribed drinking water limits through the period of study. The rest of the parameters were raised, but still less than drinking water specifications in the absence of any alternative source. Ground water quality at the outside of the ash-filled zone was apparently somewhat affected and there was no outward effect on ground water quality half kilometre away from the ash-filled region, where the ground water is used for drinking water.

Dutta et al (2009) proposed that substantial release of toxic heavy metals would occur mainly under acidic leaching circumstances. The inborn alkalinity of fly ash is not sufficient to contest this phenomenon. Since the mobility of toxic elements (except arsenic) from fly ash was slight when the final pH of the leachate was alkaline or nearly neutral, proper conditioning of coal fly ash with an proper lime dosing can offer a low cost practical solution to the refilling of surface coal mines as well as remediation of acid mine drainage.

Mishra et al. (2010) proposed that the appropriateness of Talcher coal fly ash for stowing in the nearby underground coal mines based on their physical, chemical and mineralogical study. The physical properties such as bulk density, specific gravity, particle

size distribution, porosity, permeability and water holding capacity etc. have been determined. From the chemical classification it was found that the ash samples were enhanced predominantly in Silica (SiO_2), Alumina (Al_2O_3) and Iron oxides (Fe_2O_3), along with a little amount of CaO, and fall under the Class F fly ash group. In addition, the mineral phases recognized in the ash samples were Quartz, Mullite, Magnetite, and Hematite. From the particle size and permeability approach, pond ash may be considered a better stowing material than fly ash.

Naik et al. (2012) described fly ash as a good grading material, lot of fine particles, higher specific area and low specific gravity, which easily flows through pipe to fill the mine voids in mines.

Shivpuri et al. (2012) suggested that elements in coal fly ash show fluctuating behaviour for different leaching conditions like leaching medium and pH. The fly ash may be enriched in Ca, Ni and Fe and show greater leachability in acidic or ion-exchangeable conditions. Fe is tightly bound to the ash and does not leach simply while Ca is highly soluble and leaches out in almost all mediums. Se, Cd and Ni leach out at less aggressive conditions in ion exchange able conditions, while As, Cr, Cd, Pb and Zn leach under more aggressive conditions. Also, the SO_3 content of coal fly ash may affect the leaching behaviour of fly ash as exhibited by fly Ash, which has relatively higher percentage of SO_3 and indicated different leaching trends during Sequential Extraction Procedure. Thus, toxic metal mobility is also influenced by the mode of amount of metals within the ash, especially for the metals which reduce on the surface of the particles in the furnace.

CHAPTER-3

MATERIALS AND METHODOLOGY

3.1 Introduction

The experimental program was designed to utilize the coal ash of Talcher Super Thermal Power Station (TSTPS), Kaniha, Odisha in the abandoned mine filling. For this purpose, laboratory tests have been conducted to characterize coal ash, heavy metal analysis from coal ash by leaching test and study the environmental aspects.

3.2 Material used

3.2.1 Coal ash

Ash samples were collected from Talcher Super Thermal Power Station, Kaniha. Fly ash, bottom ash was collected from the discharge point of the plant in gunny bag made of strong poly-coated cotton with 50 kg capacity. Pond ash was collected from an ash pond in 50 kg gunny bag. The mouth of each bag was immediately closed after collection and put those bags in another polypack to prevent atmospheric influences. The bags were transported with utmost care from the power plant to the laboratory and kept in a secure and controlled environment. After taking to the laboratory, the samples were screened through a 2 mm sieve, to separate out the vegetation and foreign material. The materials are stored in airtight container, for subsequent use.

3.2.2 Water sample

The three numbers of water samples were collected from near the abandoned coal mine area of Mahanadi Coal field, Talcher. The samples were collected in plastic non reacting bottles of 5 liters capacity. Immediately after collection, the bottles were recapped and sealed by the small polythene sheet and kept in a cool place till it was carried out to NIT

Rourkela for analysis. The locations of sample collected are given in Figure 3.1 and Table 3.1.

Table 3.1 Details of water sample collection

Sample No.	Sample Id	Location	Date of Collection
1	S-1	Pond 200 Meter from abandoned coal mines	19/12/2013
2	S-2	Tube well 500 Meter from abandoned coal mines	19/12/2013
3	S-3	Tube well 1 K.M. from abandoned coal mines	10/12/2013

(1)

(2)

(3)

Figure 3.1 Sample collection

3.3 Experimental Procedure

3.3.1 Specific Gravity Test (By Density Bottle Method) IS: 2720 (Part-III/SEC-I)

Specific gravity is defined as the ratio of the weight in air of a given volume of a material at a specified temperature to the weight in air of an equal volume of distilled water at a specified temperature. The purpose of the test is to define the specific gravity of soil passing the 4.75 mm sieve by density bottle method.

50g of sample of fly ash is taken in each 3 bottles and added to distilled water; the weight of the water + bottle is taken. Then all the 3 bottles are subjected to sand bath, heating is done up to air bubbles are seen in the bottle. This is done to remove the entrapped air in the mixture; the bottle is kept for around 1 hour so that the temperature comes to 27^{o}C.

Calculation:

$$\text{Specific Gravity, } G = \frac{W_2 - W_1}{(W_2 - W_1) - (W_3 - W_1)}$$

Where

W_1= Wt. of density bottle in gm

W_2=Wt. of bottle with dry soil in gm

W_3=Wt. of bottle with soil and water in gm

W_4=Wt. of bottle full of water in gm

3.3.2 Grain Size Analysis (By Sieve Analysis and Hydrometer Analysis) IS: 2720 (Part-IV)

3.3.2.1 Sieve analysis

Sieving is conducted by arranging the various sieves over one another in order of their mesh openings biggest aperture at the top and smallest at the bottom. A holder is kept at the bottom and a cover is put at the top of the whole setup. The soil is put through the top sieve and adequate amount of shaking is done to let the soil particles pass through the various

sieves. 4.25mm, 2mm, 1mm, 425 micron, 150 micron and 75 micron IS sieves were used to perform the sieving.

The results of sieve analysis are plotted on a graph of percentage passing versus the sieve size. On the graph the sieve size scale is logarithmic. To find the percentage of cumulative passing through each sieve, the percentage retained on each sieve is found. The following equation is used for this:

$$\% \text{ Retained} = \frac{W_{Sieve}}{W_{Total}} X100$$

Where W_{Sieve} = the weight of aggregate in a particular sieve

W_{Total} = the total weight of the aggregate.

After this the cumulative percentage of aggregate retained in a sieve is found. To do so, the total amount of aggregate that is retained on each sieve and the amount in the previous sieve are added up. The cumulative percentage passing of the aggregate is found by subtracting the percentage retained from 100%.

The values are then plotted on a graph with cumulative percentage passing on the y axis and logarithmic sieve size on the x axis.

3.3.2.2 Hydrometer analysis

This process defines the quantitative determination of the distribution of particle sizes in soils. The distribution of particle sizes larger than 75 μm is determined by a sedimentation process, by means of a hydrometer to secure the essential data.

Dispersing agent – Sodium metaphosphate solution is prepared in distilled or demineralized water. 40gm of sodium hexametaphosphate/liter is used in the solution.

About 50gm of fly ash is taken and added with water and sodium hexametaphosphate and put into the mechanical stirring cup. Stirring process occurs for a period of 15 minutes. After that it is poured into the hydrometer flask.

After 20 seconds the Hydrometer is inserted gently to a depth slightly below its floating position.

Hydrometer readings are taken in the interval of ½, 1, 2,4,8,15,30 minutes, 1, 2, 4,8,16 and 24 hours. After that it was taken out and rinse with distilled water.

The hydrometer was re-inserted in the suspension and readings were taken over periods of 8, 15, and 30 minutes; 1, 2, 4, 8, 16 and 24 hours after shaking. The hydrometer is removed and rinsed with water after each reading.

3.3.3 Water holding capacity of coal ash

Keen's Box Apparatus (Figure 3.2) was used in the experiment consisting of a brass box (diameter approximately 5 cm and height 1.6 cm) with a perforated base.

Suitable filter paper was placed in the perforated base of the Keen's box and weighed in a physical balance. The keen's box was filled with soil by adding small quantities at a time and tapping the box after each addition to ensure uniform packing. Surplus soil is stricken with a sharp blade. The box was kept in a small tray, which contained water up to ¼ inch and left for a night. At the end of the period, the box was removed and its outside was wiped with a dry cloth and weight was taken immediately. The box containing the wet soil was placed in an oven and the soil was dried at 105^0 C till a constant weight was obtained. The amount of water absorbed by the filter paper was determined by taking 10 pieces of filter paper together, weighing as such, and then saturating with water and weighing again. This moisture absorbed by each filter paper (m) can be determined.

Calculation

Weight of box + filter paper = a gm

Weight of box + filter paper + oven dry soil = b gm

Weight of box + wet filter paper + saturated soil=c gm

Max. water holding capacity of soil = $\frac{c-(b+m)}{b-a} * 100$

Figure 3.2 Keen's Box Apparatus

3.3.4 BET specific surface area test (IS 11578 – 1986)

This test is established by Brunauer, Emmett, and Teller in 1938. The specific surface area is defined as the ratio A/m (unit: m^2/gm) between the total surface area of a solid and its mass (sample weight). The surface area contains all parts of accessible inner surfaces (mainly pore wall surfaces).

A small amount of the sample was taken on the tube and the tube was placed in a Dewar flask containing liquid nitrogen (Liq. N_2). Initially the sample was degasified to remove the impurities and gases. Then gaseous nitrogen was passed through the sample and based on adsorption of the gas, the surface area of the sample was calculated.

This procedure is based on, Brunauer Emmett Teller, (BET) which explain the physical attraction of gas molecules on its solid surfaces, which is based on important analysis for measurement of the specific surface area of material. The conception of this theory is the extension of Langmuir theory, which says that, gas molecule monolayer adsorption to multilayer adsorption. This hypothesis is based on (i) the gas molecules physically adsorbed to the solid surfaces infinite no of pores. (ii) There is no interaction

between each layer of adsorption. (iii) After, that Langmuir theory can be applied to each layer. The specific surface of powder or powder porous material, quantity of nitrogen covers the surface of solid area, is calculated independently in accordance with IS: 11578-1986. The number of such gas molecules, multiplied by the area of each molecule of contact surface gives the total area per unit material.

3.3.5 X-Ray Diffraction of coal Ash

The X-ray diffraction technique gives the idea about the structure of the materials which is a key requirement for understanding material properties. The process of ash formation controls or retards the morphology and crystal growth of minerals. Even though fly ash is regarded as an amorphous Ferro alumina silicate material, the X-ray diffraction spectra of different fly ash indicate that they contain both crystalline and amorphous phases of materials. The samples were dried at 105^{o}C and mainly taken into powered form for X-ray diffraction analysis. X-ray powder diffraction was firstly carried out on the powders for qualitative identification of mineral phases. The sample was analysed by passing through a Philips diffractometer with a Cu K (radiation source and single crystal graphite monochromatic. An angular range of 10^{o}-80^{o} of 2ϕ value in 0.50^{0} increments was used throughout.

3.3.6 Scanning Electron Microscope (SEM) AND Energy Dispersive X-Ray Spectroscopy (EDS) of coal ash

A scanning electron microscope (SEM) is a kind of electron microscope that gives picture of a sample by scanning it with an absorbed beam of electrons. The electrons interrelate with electrons in the sample, creating several signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is usually scanned in a raster scan form, and the beam's position combines with the identified signal to produce an image. SEM can achieve resolution better than 1 nanometre.

Specimens can be observed in high vacuum, low vacuum and in environmental conditions. SEM specimens can be observed in wet conditions.

Energy dispersive x-ray spectroscopy is an analytic technique used for the characterization of chemical constituent in the sample. It uses the x-ray spectrum emitted by the specimen sample bombarded with a beam of electrons for chemical characterization. All elements ranging from atomic number 4 to 92 can be detected by EDS method. Qualitative analysis involves the identification of the spectral lines. Quantitative analysis entails measuring line intensities meant for each element in the sample and for the same elements in calibration standards of known composition. In the present study SEM, JOEL, JSM840A (Japan) have been used with the gold plated sample.

3.3.7 Batch Leaching Test (ASTM- D 4793-09)

For the batch leaching test, required liquid/ solid (L/S) ratio of 5, 10, 20, 50 and 100 have been considered. Hence three 5gm samples of fly ash (as it is, without drying) in three conical flask bottles were taken and 50ml extracting reagent (deionized water in case of our leaching experiments) was added to each bottle. A stirring was performed on a rotary shaker (Figure 3.3) for 24 hours. After extraction, the extracts were separated from the solid residue by filtration through a Whatman No.42 filter paper (Figure 3.4). Five drops of 1 N Nitric acid (HNO_3) were added to it, to avoid the precipitation of some extracted metals as their hydroxides on storage and extracts were stored in a refrigerator (4^oC) until metal determination. The metal concentrations were determined by AAS (Atomic Absorption Spectrometer). This was repeated three times for triplicate estimation.

Figure 3.3 Rotary Flask Shaker

Figure 3.4 Sample Extraction Procedure

3.3.8 Toxicity Characteristic Leaching Procedure (USEPA-TCLP Method 1311)

The Toxicity Characteristic Leaching Procedure needs the use of an extraction fluid made of buffered acidic medium to run the experiment. 1 M sodium acetate buffer was used as an extraction liquid; pH has been maintained 5±0.01 as per United States Environment Protection Agency (USEPA) procedure. A 5 gm fly ash sample was taken and then extraction fluid equal to 20 times the amount of sample taken was added to it. The system was tightly closed and then placed on the rotating shaker (Figure 3.3) for 18 hours, rotating at 30 ±2 RPM at a room temperature of about 25^0C. Triplicate extractions have been performed using the same mass of the sample and the same volume of the extracting agent. Heavy metal analysis was carried out on AAS and the results are expressed as averages of the results of triplicate estimation. Till the metal analysis is completed the sample was stored in the refrigerator at 4^0C.

3.3.9 pH of coal ash (IS 2720 (Part 26))

The coal ash samples were sieved through 425-micron IS sieve before pH test. 50gm of the ash sample was taken in 250-ml beaker. 125 ml of distilled water was added to it. The suspension was stirred for a few seconds. The beaker was covered with a cover glass and allowed to stand for one hour, with occasional stirring. Then the water sample was extracted from the beaker with the help of Whatman filter paper of 42 No. Then the collected sample was taken for pH measurement by pH meter.

3.3.10 Coal ash slurry

The coal ash sample and normal water were mixed in a beaker with a proportion of 1:10 and kept for 24 hours in rotary shaker. Then slurry was prepared. Then slurry and mine water (near the abandoned mine) mix has been tested with 1:1 and 1:2 proportion in rotary shaker. For pH test, slurry and slurry mine water mix was filtered with Whatman paper No.42 and the sample was collected.

3.3.11 pH value (electrometric methods) (IS 3025 (Part-11))

The pH of a liquid solution is determined as the negative logarithm of hydrogen ion concentration. At a given temperature, the concentration of the acidic or basic character of a solution is indicated by pH or hydrogen ion concentration. pH values from 0 to 7 are falling in acidic, 7 to 14 falling in alkaline and 7 is neutral. pH value is governed largely by the carbon dioxide/ bicarbonate/ carbonate equilibrium. It may be affected by human substances, by changes in the carbonate equilibriums due to the bioactivity of plants and in some cases by hydrolysable salts. It is used in several calculations in analytical work and its adjustment to an appropriate value is absolutely necessary in many of the analytical procedure.

Calibration

Calibrate the electrode system against standard buffer solution of known pH. Use distilled water of a conductivity of less than 2μ Siemens at 25°C and pH 5.6 to 6.0 for the preparation of all standard solutions. For unchanging investigation, commercially presented buffer tablets, powders or solutions of testing quality also are allowed. Buffer having pH 4.0, 7.0 and 9.2 are available. In making buffer solutions from solid salts, all the material is melted in it; otherwise, the pH calibration will be improper. The electrode system with buffer solutions have been prepared and standardized with a pH similar to that of the sample, to minimize error resulting from nonlinear response of the electrode.

Procedure

- Electrodes after storage solutions were removed and washed with distilled water.
- Electrodes were dry by softly staining with a soft tissue paper; standardize the instrument with electrodes deep in a buffer solution within 2 pH units of sample pH.
- Electrodes were detached from the buffer, washed thoroughly with distilled water and stained dry.

- Electrodes were immersed in a second buffer below pH 10, around 3 pH units different from the first. It must be taken care that the reading must be within 0.1 units for the pH of second buffer.
- For sample analysis, balance was established between the electrodes and sample by stirring the sample to confirm homogeneity and measure pH.
- For buffered samples, the electrodes were conditioned after cleaning by dropping them into the same sample, and reading pH.
- With poorly buffered solutions, electrodes were calibrated by dipping in three or four successive portions of samples.
- The pH value was obtained directly from the instrument (Figure 3.5).

Figure 3.5 pH Meter

3.3.12 Measurement of Turbidity (IS 3025 (Part-10))

Turbidity can be determined by its effect on the scattering light, which is termed as Nephelometry. Turbiditimeter can be used for sample with moderate turbidity and nephelometer for sample with low turbidity. The higher intensity of scattered light, higher the turbidity. Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample. The standard

method for the determination of turbidity has been based on the Jackson candle turbidity meter. An indirect method is necessary to estimate the turbidity in the range of 0-5 units; the turbidity of treated water generally falls in this range. Most commercial turbidity meters available for measuring low turbidity give comparatively good indicators of the intensity of light scattered in one particular direction, predominantly at right angle to the incident light. Results of Nephlometric measurements are expressed as Nephelometric Turbidity units (NTU). The NTU value is directly obtained from the instrument (Figure 3.6)

Figure 3.6 Turbidity Meter

3.3.13 Measurement of Total Suspended Solids (IS 3025 (Part-17))

The residue left after the disappearance and successive drying in oven at specific temperature 103-105°C of a known volume of sample are total solids. Total solids include "Total Suspended Solids (TSS)" and "Total Dissolved Solids (TDS)". Whereas loss in weight on ignition of the same sample at 500°C, 50°C, in which organic matter is converted to CO_2 volatilisation of inorganic matter as much as consistent with complete oxidation of organic matter, are volatile solids.

Procedure

- A known volume of a well-mixed sample in a tarred dish ignited to constant weight (W_1) was taken.
- The sample was evaporated to desiccation at 103-105°C for 24hrs.
- Next the sample was cool in a desiccator and it was weighed and reading was recorded (W_2).
- The dish was burnt for 15-20 minutes in a muffle furnace maintained at 550±50°C.
- The dish was partly cooled in air until most of the heat was dissipated, and then transferred to a desiccator for final cooling in a dry atmosphere and final weight (W_3) was noted.
- The concentration was calculated in percentage by weight.

Calculation

The total and the unstable solids are expressed as:

Total solids, $mg/L = (W_2 - W_1) \times 1000/mL$ of sample

and

$(W_2 - W_3) \times 1000/mL$ of sample

Where W_1, W_2 and W_3 are noted on mg.

3.3.14 Measurement of Total Hardness (EDTA method) (IS 3025 (Part-21))

Hardness is determined by the EDTA method by alkaline condition; EDTA and its sodium salts from a soluble chelated complex with certain metal ions. Calcium and Magnesium ions develop wine red colour with Eriochrome black T in aqueous solution at pH 10.0 ± 0.1. When EDTA is added as a titrant, Calcium and Magnesium divalent ions get complexes resulting in a sharp change from wine red to blue which indicates endpoint of the titration. Magnesium ion must be present to yield satisfactory point of the titration. A small

amount of complexometically neutral magnesium salt of EDTA is added to the buffer. At a higher pH, i.e. at about 12.0 Mg^{++} ions precipitate and only Ca^{++} ions remain in solution. At this pH murexide (Ammonium Purpurate) indicator forms a pink color with Ca^{++}. When EDTA is added Ca gets complexes resulting in a change from pink to purple, which indicates the end point of the reaction.

Procedure

- 25 or 50mL of well mixed sample was taken in a conical flask.
- 1-2mL of buffer solution was added, followed by 1mL inhibitor.
- A pinch of Eriochrome black T was added and titrated with standard EDTA (0.01M) till wine red colour turn to blue, the required volume of EDTA (X) was noted down.
- Ammonium Purpurate was added and the volume of EDTA (Y) was noted down.
- Volume of EDTA required by sample, A = (X-Y) was calculated.
- For natural waters of low hardness, a larger sample volume, i.e. 100-1000mL should be taken for titration and proportionally larger amounts of buffer, inhibitor and indicators should be added. Standard EDTA titrant should be slowly added from a micro burette and run a blank using redistilled, deionized water of the same volume as a sample. Blank correction is applied for computing the results.

Calculation

Total Hardness as $CaCO_3$ $mg/L = (A \times B \times 1000/mL$ of sample

Where, A= volume of EDTA required by sample

B= mg $CaCO_3$ equivalent to 1mL EDTA titrant

3.3.15 Methodology for measurement of Alkalinity (IS 3025 (Part-23))

Sample preparation

Alkalinity of the sample can be determined by titrating with standard sulphuric acid (0.02N) at room temperature using phenolphthalein and methyl orange indicator. Titration to

decolourisation of phenolphthalein indicator will indicate complete neutralization of OH^- and ½ of CO_3^{--}, while sharp change from yellow to orange of methyl orange indicator will indicate total alkalinity (complete neutralization of OH^-, CO_3^{--}, HCO_3^-).

Procedure

3.3.15.1 Indicator method

20ml or a suitable amount of sample is pippeted into 100 ml beaker. If the pH of the sample is over 8.3, then 2 or 3 drops of phenolphthalein indicator are added and titrated with a standard sulphuric acid solution till the pink colour observed by indicator just disappears. The volume of standard sulphuric acid solution used is recorded. About 2 to 3 drops of indicator is mixed into the solution in which the phenolphthalein alkalinity has been determined. This is titrated with the standard acid to light pink colour (equivalent of pH 3.7). The volume of standard acid used after phenolphthalein alkalinity is recorded.

3.3.15.2 Potentiometer method

In a pipette, 20 ml or a suitable amount of sample is taken and titrated with standard sulphuric acid to pH 8.3 and then to pH 3.7, using a potentiometer. No indicator is required.

Calculation

Phenolphthalein alkalinity (as mg/L of $CaCO_3$) = $\frac{A \times N \times 50000}{V}$

Total alkalinity (as mg/L of CaCO3) = $\frac{(A+B) \times N \times 50000}{V}$

Where,

A= ml of standard sulphuric acid used to titrate to pH 8.3,

B= ml of standard sulphuric acid used to titrate from pH 8.3 to pH3.7

N=normality of acid used, and

V=Volume in ml of sample taken for test.

3.3.16 Atomic Absorption Spectrometer test

Atomic absorption spectrometer (Figure 3.5) is used for detecting metals in solution. The sample is fragmented into very small drops (atomized). It is then fed into a flame. Isolated metal atoms interact with radiation that has been pre-set to certain wavelengths. This interaction is measured and interpreted. Atomic absorption exploits different radiation wavelengths absorbed by different atoms.

Figure 3.7 Atomic Absorption Spectrometer

The instrument is most reliable when a simple line relates absorption-concentration. Atomizer or flame and monochromator instruments are key to making the AAS device work. Relevant variables of AAS include flame calibration and unique metal based interaction.

CHAPTER-4

RESULTS & DISCUSSION

4.1 Introduction

The experiments have been conducted on coal ash collected from Talcher Super Thermal Power Station (TSTPS), Kaniha, Odisha for abandoned mine filling. The analysis of results is discussed in details in the following paragraphs.

4.2 Specific Gravity of coal ash

The specific gravity of Indian coal ash lies between 2.06-1.64 (Pandian et al. 1998) which is much less than soil. The specific gravity of collecting sample fly ash is higher than pond ash and bottom ash. The value of TSTPS coal ash with distilled water as pore medium is given in Table 4.1

Table 4.1 Specific gravity (*G*) of coal ash

Ash Type	Specific Gravity (*G*)	Specific Gravity (Pandian et al., 1998)
Fly ash	2.05	2.06-1.70
Bottom Ash	1.95	2.05-1.73
Pond Ash	1.92	2.05-1.64

4.3 Particle size distribution of coal ash

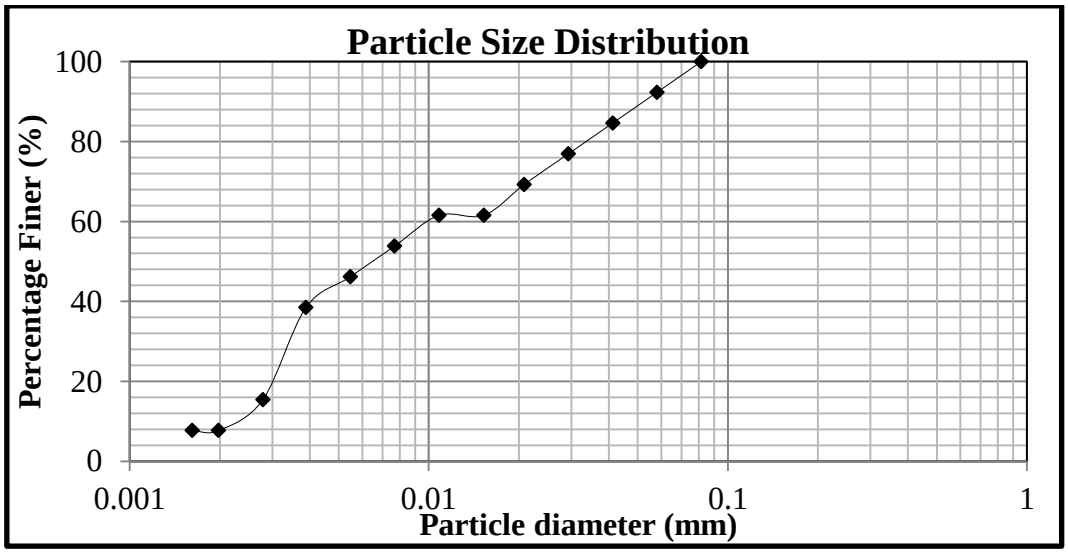

Figure 4.1 Particle Size distribution curve of fly ash

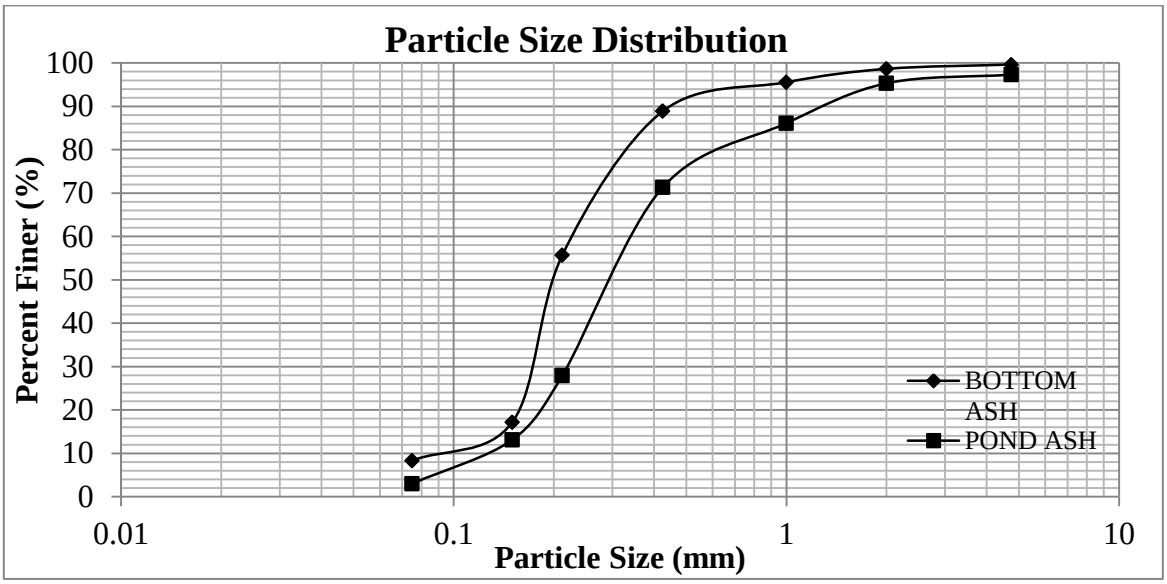

Figure 4.2 Particle Size distribution curves of bottom ash and pond ash

Table 4.2 Grain size distribution of coal ash

Ash Type	Clay %	Silt %	Sand %	C_c	C_u
Fly Ash	50%	23%	17%	0.11	6.54
Bottom Ash	-	-	100%	2.21	1.72
Pond Ash	-	-	100%	2.5	1.03

From the grain size distribution curve (shown in Figure 4.1 and 4.2 and Table 4.2), fly ash is fine grained substances consisting of silt and clay. Bottom ash and pond ash are poorly graded sand.

4.4 Water Holding Capacity of Coal Ash

The water holding capacity of coal ash is given in Table 4.3

Table 4.3 Water holding capacity of coal ash

Ash Type	Water Holding Capacity, %
Fly Ash	59.90
Bottom Ash	77.34
Pond Ash	68.76

From the Table 4.3 it shows that Bottom ash has more water holding capacity than Pond ash and Fly ash. The bottom ash is coarser than pond ash and fly ash. The bottom ash is coarser than pond ash and fly ash. So water holding capacity is a function of particle size of coal ash. The sample holding greater amount of fine particles has less water holding capacity. So bottom ash will absorb more water after filling and allow the least amount of water to the ground.

4.5 X-Ray diffraction of coal ash

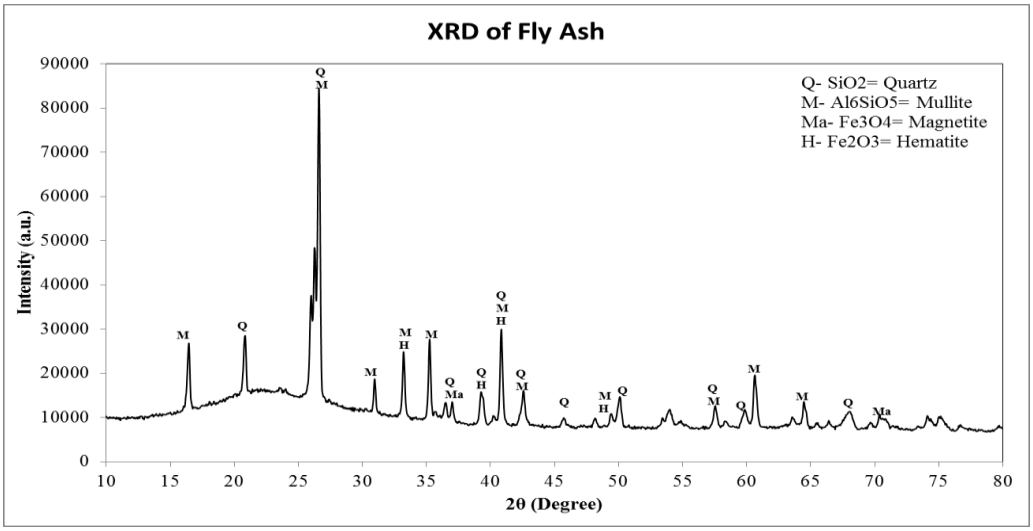

Figure 4.3 XRD graph of fly ash

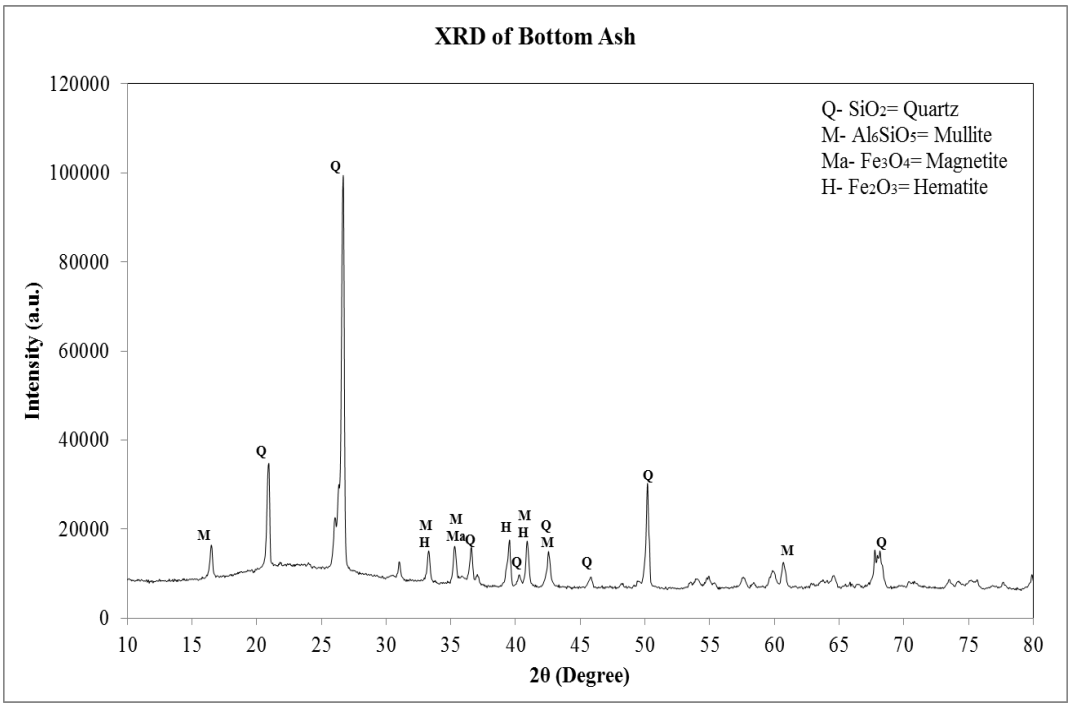

Figure 4.4 XRD graph of bottom ash

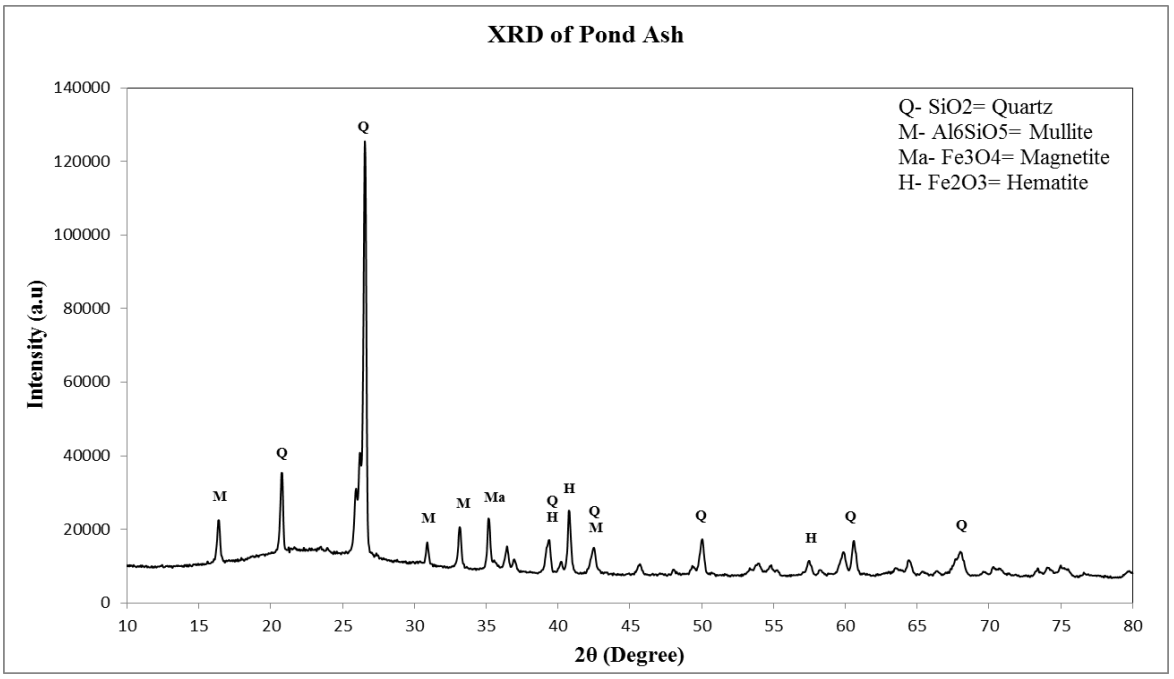

Figure 4.5 XRD graph of pond ash

The XRD outlines of the fly ash, pond ash and bottom ash (shown in Figure 4.3, 4.4 & 4.5) samples have specific peaks of quartz (SiO_2), mullite ($Al_6Si_2O_{13}$) and iron oxides such as magnetite (Fe_3O_4) and hematite (Fe_2O_3) which arise in crystalline form.. In all the ash samples, the most extreme $2\theta=26.66^0$ is known as the main peak due to quartz. The occurrence of heavy minerals like magnetite and hematite are showed by their individual peaks. The most common phases and minerals found in the ash samples contain quartz and mullite. The amount of quartz increases the strength of coal ash. So after filling the abandoned coal the place can be used for public use.

4.6 Morphology of coal ash

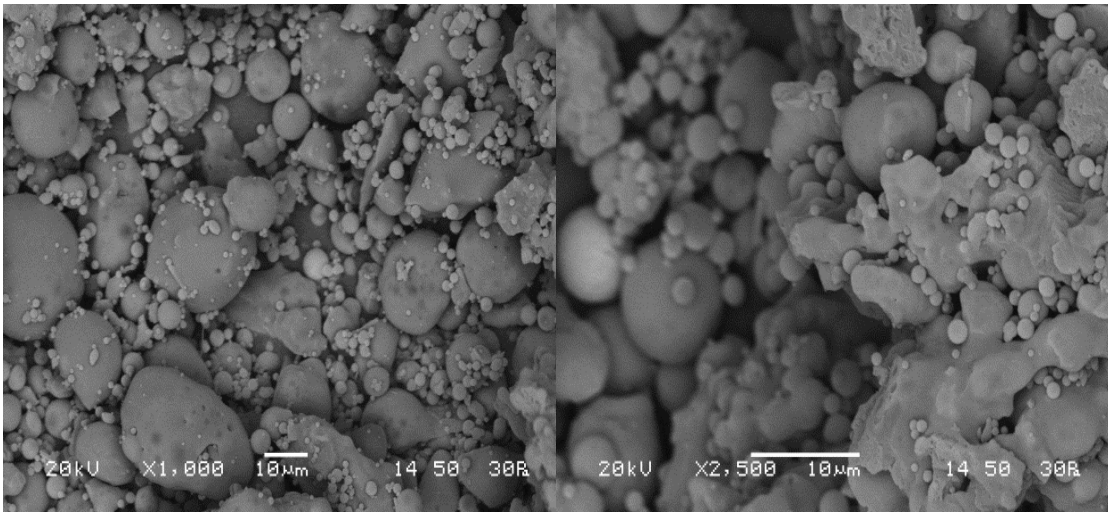

Figure 4.6 SEM photography of fly ash at 1000X and 2500X

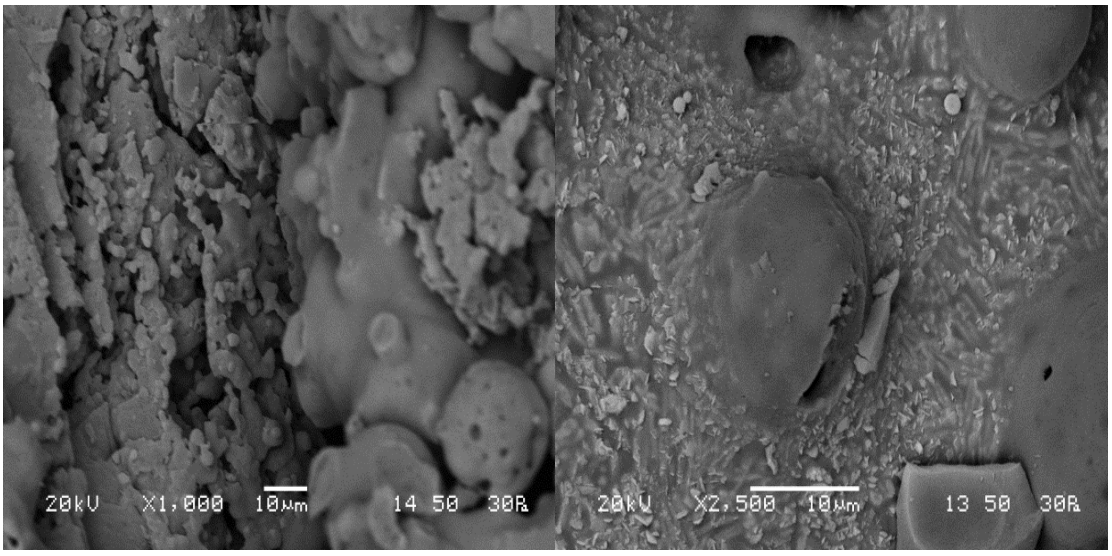

Figure 4.7 SEM photography of bottom ash at 1000X and 2500X

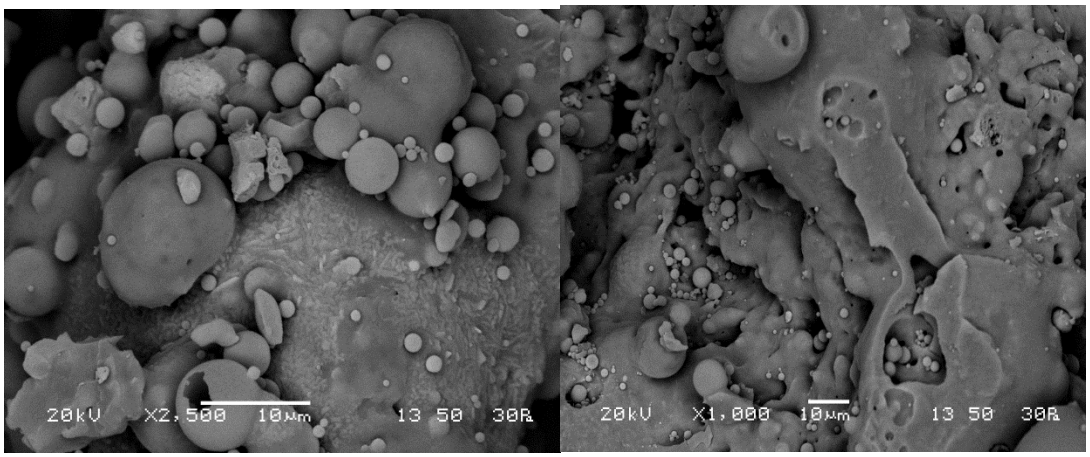

Figure4.8 SEM photography of pond ash at 1000X and 2500X

The SEM (Figure 4.6, 4.7 and 4.8 shows) shows that fly ash samples are sphere-shaped and the brighter particles are cenosphere. In bottom ash, it shows the particles are hollow spherical and plate like structures is there. Pond ash consists of both hollow, spherical and plate like structures. The spherical morphology of the fly ash and pond ash creates the ball-bearing effect which affects a frictionless flow in the pipe with low wear and tear. So the pond ash and fly ash is good for filling in an abandoned mine.

4.7 Compositional analysis of coal ash

4.7.1 Chemical composition (wt. %) of fly ash

The chemical composition of fly ash is given in Table 4.4.

Table 4.4 Chemical composition of fly ash

Compound	Percentages (%)
SiO_2	41.24
Al_2O_3	24.17
Fe_2O_3	5.58
Na_2O	0.53
K_2O	2.15
MgO	0.76
TiO_2	2.09
SO_3	1.07
Zr_2O_3	22.38
LOI	0.13

From the Table 4.4, $SiO_2+Al_2O_3+Fe_2O_3=41.24+24.17+5.58=70.99\%$

4.7.2 Chemical composition (Wt. %) of bottom ash

The chemical composition of bottom ash is given in Table 4.5.

Table 4.5 Chemical composition of bottom ash

Compound	Percentages (%)
SiO_2	35.83
Al_2O_3	17.51
Fe_2O_3	35.19
Na_2O	0.81
K_2O	1.02

Compound	Percentages (%)
MgO	0.81
TiO_2	2.31
P_2O_5	2.30
CaO	1.10
SO_3	0.34
LOI	2.78

From the Table 4.5, $SiO2+Al_2O_3+Fe_2O_3$=35.83+17.51+35.19=88.57%

4.7.3 Chemical composition (Wt. %) pond ash

The chemical composition of pond ash is given in Table 4.6.

Table 4.6 Chemical composition of pond ash

Compound	Percentages (%)
SiO_2	55.21
Al_2O_3	27.93
Fe_2O_3	3.58
TiO_2	3.85
K_2O	1.63
MgO	1.04
P_2O_5	2.96
CaO	0.82
SO_3	0.32
LOI	2.66

From the Table 4.6, $SiO_2+Al_2O_3+Fe_2O_3$=55.21+27.93+3.58=86.72%

From the entire Table (4.4, 4.5 and 4.6) it was found that $SiO_2+Al_2O_3+Fe_2O_3$ >70%, as per ASTM-618, the coal ash was Class ‘F’ coal ash. Class ‘F’ coal ash is a better filler material than Class ‘C’ fly ash.

4.8 Specific Surface Area of Coal Ash

The specific surface area of coal ash is given in Table 4.7.

Table 4.7 Specific surface area of coal ash

Ash Type	Fly Ash	Bottom Ash	Pond Ash
SSA (m^2/Kg)	229.5	153.4	186.7

The specific surface area of Indian coal ashes is in between 130-530 m^2/Kg (Sridharan et al., 2000). It concludes that if more in specific gravity and finer ash particles, then more the specific surface area value.

4.9 pH of Coal Ash

The pH of coal ash is given in Table 4.8

Table 4.8 pH of coal ash

Ash Type	Fly Ash	Bottom Ash	Pond Ash
pH	7.21	6.90	7.01

Table 4.9 pH range of coal ash (Hajarnavis 2000)

pH	Class
<4.0	Highly Acidic
4.0 – 6.5	Moderately Acidic
6.5 – 7.5	Slightly Acidic

From the result of pH (shows in Table 4.9) value it is found that the coal ash of TSTPS is slightly acidic in nature.

4.10 Leaching Analysis of Coal Ash

4.10.1 Batch Leaching Test of coal ash

4.10.1.1 For L/S=100

Table 4.10 Heavy metal concentration of coal ash in L/S=100

Metals	Fly ash	Bottom ash	Pond ash
Iron	2.129 ppm	0.91 ppm	0.998 ppm
Copper	0.098 ppm	0.019 ppm	0.017 ppm

Metals	Fly ash	Bottom ash	Pond ash
Magnesium	5.597 ppm	3.17 ppm8	2.997 ppm
Zinc	4.987 ppm	2.989 ppm	1.789 ppm
Lead	ND	ND	ND
Nickel	ND	ND	ND

ND: - Not Detected

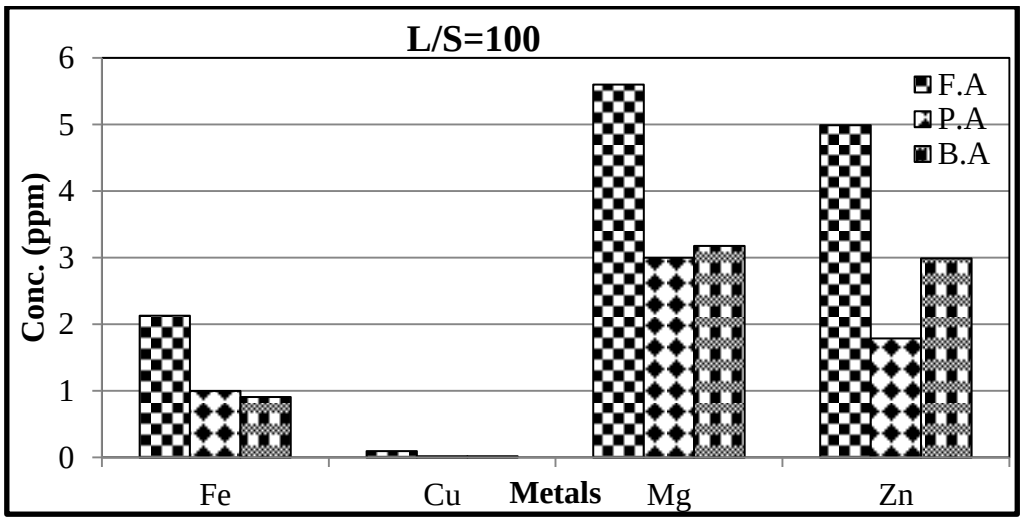

Figure 4.9 Heavy metal Concentration of coal ash in L/S=100

From the Table 4.10 it is clear that maximum absorption of metals comes from Fly ash as compared to Bottom ash and Pond ash.

4.10.1.2 For L/S=50

Table 4.11 Heavy metal concentration of coal ash in L/S=50

Metals	Fly ash	Bottom ash	Pond ash
Iron	3.419 ppm	1.049 ppm	1.029 ppm
Copper	0.298 ppm	0.039 ppm	0.029 ppm
Magnesium	5.879 ppm	3.926 ppm	3.059 ppm
Zinc	5.119 ppm	3.019 ppm	1.987 ppm
Lead	ND	ND	ND
Nickel	ND	ND	ND

ND: - Not Detected

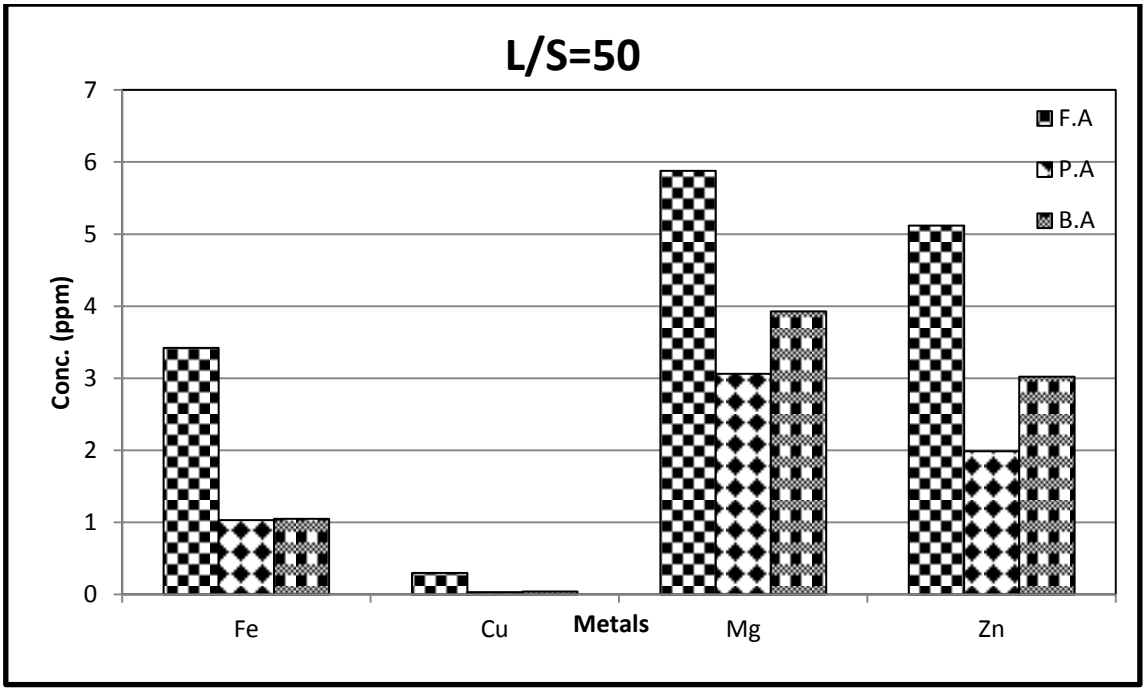

Figure 4.10 Heavy metal concentration of coal ash in L/S=50

4.10.1.3 For L/S=20

Table 4.12 Heavy metal concentration of coal ash in L/S=20

Metals	Fly ash	Bottom ash	Pond ash
Iron	4.059	1.159	1.129
Copper	0.319	0.137	0.049
Magnesium	6.019	4.89	3.397
Zinc	5.369	3.158	2.168
Lead	ND	ND	ND
Nickel	ND	ND	ND

ND: - Not Detected

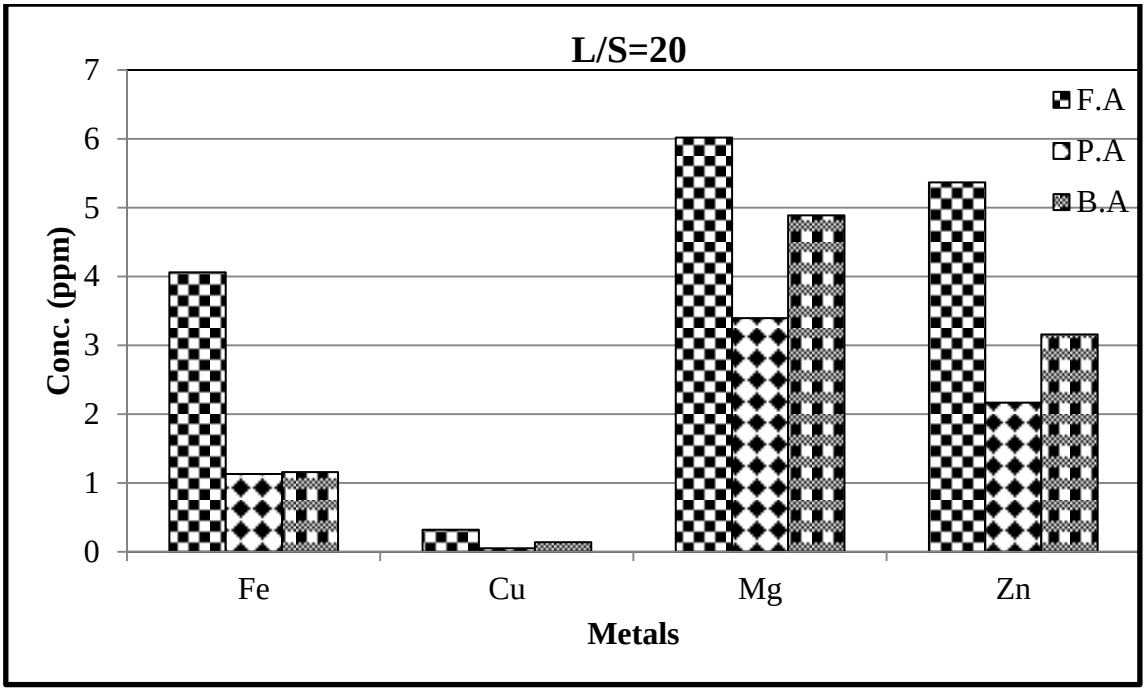

Figure 4.11 Heavy metal concentration of coal ash in L/S=20

4.10.1.4 For L/S=10

Table 4.13 Heavy metal concentration of coal ash in L/S=10

Metals	Fly ash	Bottom ash	Pond ash
Iron	4.979 ppm	1.258 ppm	1.917 ppm
Copper	0.398 ppm	0.149 ppm	0.053 ppm
Magnesium	6.978 ppm	5.578 ppm	3.567 ppm
Zinc	6.019 ppm	3.575 ppm	2.352 ppm
Lead	ND	ND	ND
Nickel	ND	ND	ND

ND: - Not Detected

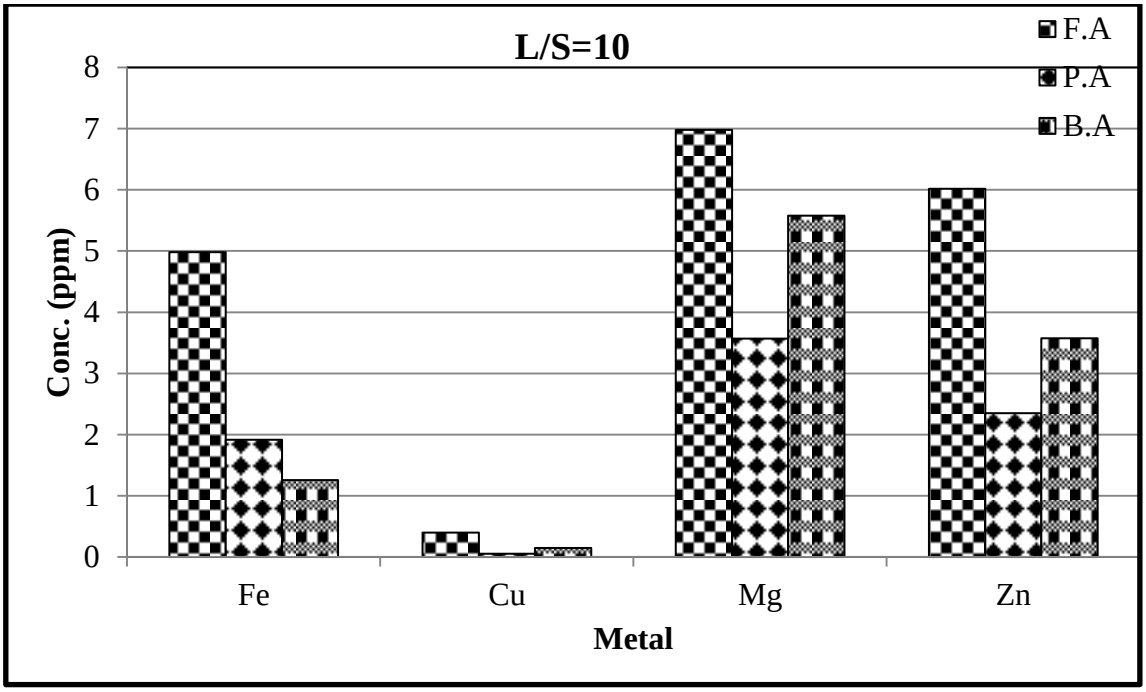

Figure 4.12 Heavy metal concentration of coal ash in L/S=10

4.10.1.5 For L/S=5

Table 4.14 Heavy metal concentration of coal ash in L/S=5

Metals	Fly ash	Bottom ash	Pond ash
Iron	5.111 ppm	1.358 ppm	2.023 ppm
Copper	0.413 ppm	0.168 ppm	0.072 ppm
Magnesium	7.092 ppm	7.094 ppm	3.754 ppm
Zinc	6.238 ppm	3.984 ppm	2.572 ppm
Lead	ND	ND	ND
Nickel	ND	ND	ND

ND: - Not Detected

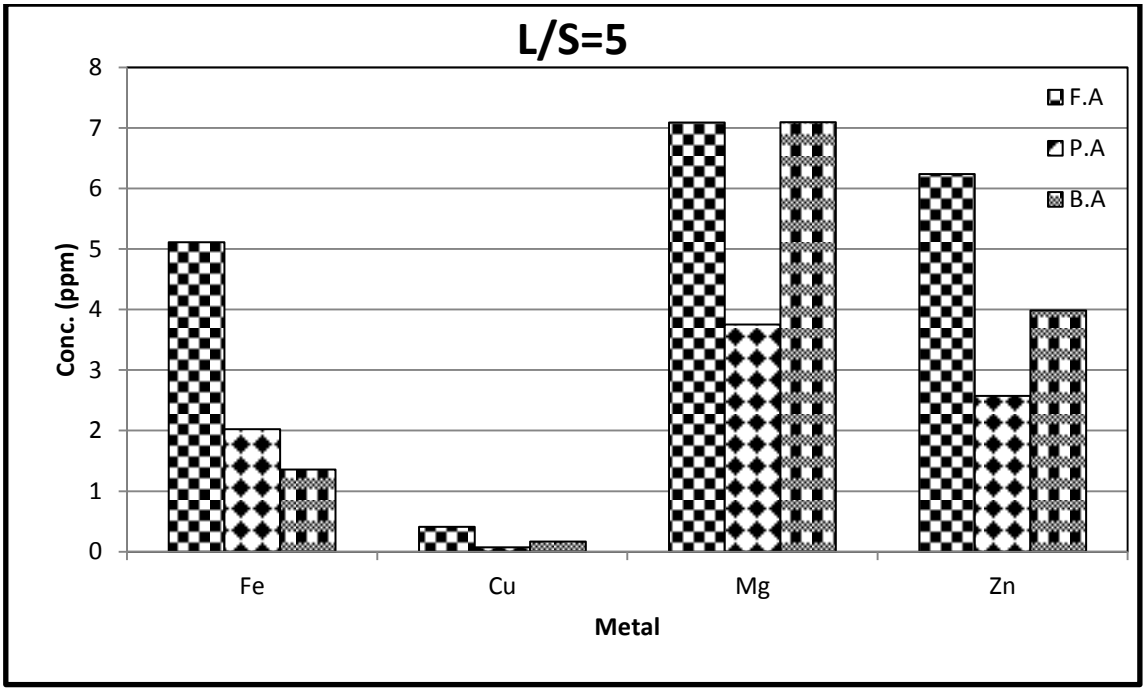

Figure 4.13 Heavy metal concentration of coal ash in L/S=5

4.10.1.6 Comparison between fly ash, bottom ash and pond ash

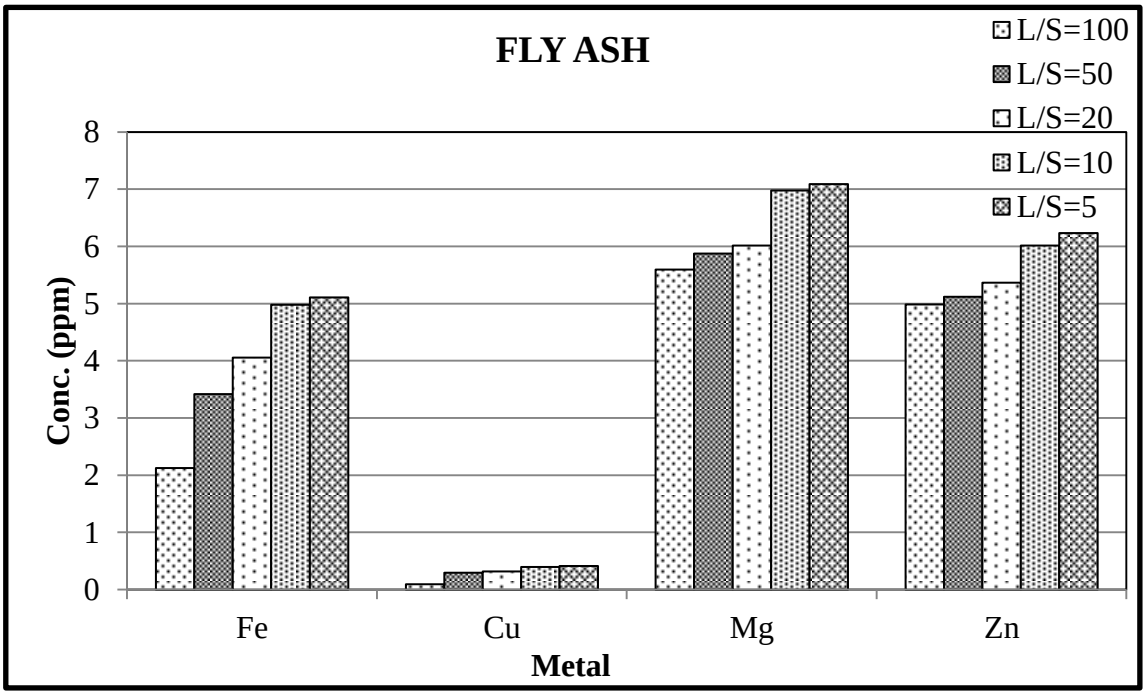

Figure 4.14 Total heavy metals leached from fly ash

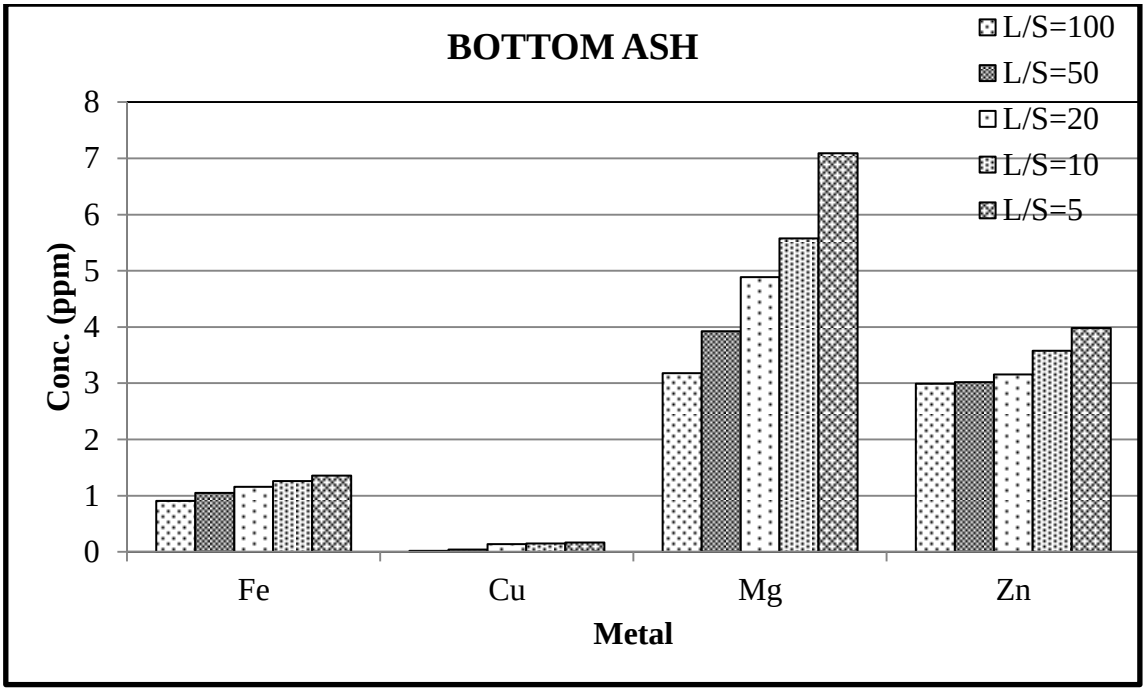

Figure 4.15 Total heavy metals leached from Bottom ash

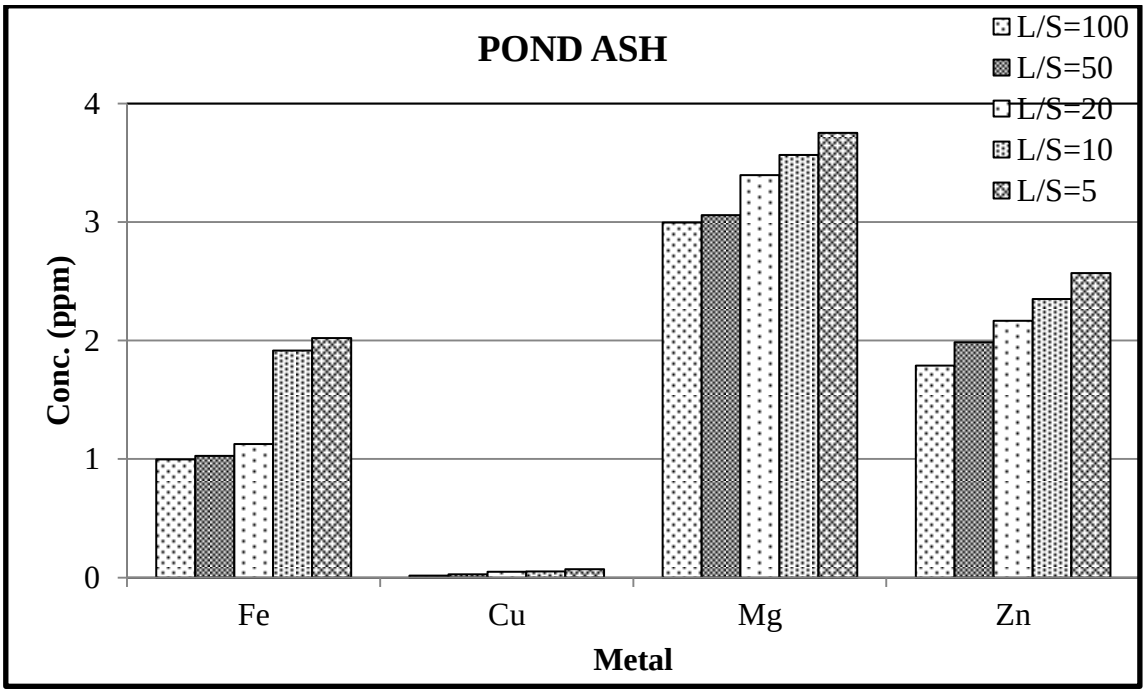

Figure 4.16 Total heavy metals leached from Pond ash

The results of heavy metals concentration found from batch leaching test in different liquid – solid ratio are shown in Table 4.10 to 4.14 and Figures 4.9 to 4.16. Lead and Nickel did not leach from the coal ash sample. Magnesium and Zinc show solubility with deionized water and leached in higher concentration in all samples of coal ash. The leached copper

concentration was low in comparison to magnesium; this is probably because copper is precipitated as their insoluble hydroxides. Concentration of metals increases with the decrease of liquid to solid ratio. So leaching of heavy metal concentration is inversely proportional to liquid to solid ratio (L/S).

4.10.2 Toxicity Characteristic Leaching Procedure (TCLP) method

Table 4.15 Heavy metal concentration of coal ash in TCLP method

Metals	Fly ash	Bottom ash	Pond ash
Iron	2.05 ppm	2.32 ppm	1.21 ppm
Copper	7.15 ppm	5.48 ppm	8.16 ppm
Magnesium	239.97 ppm	186.68 ppm	167.59 ppm
Zinc	1.58 ppm	1.98 ppm	0.99ppm
Lead	0.89 ppm	ND	ND
Nickel	0.34 ppm	0.55 ppm	1.16 ppm

ND: - Not Detected

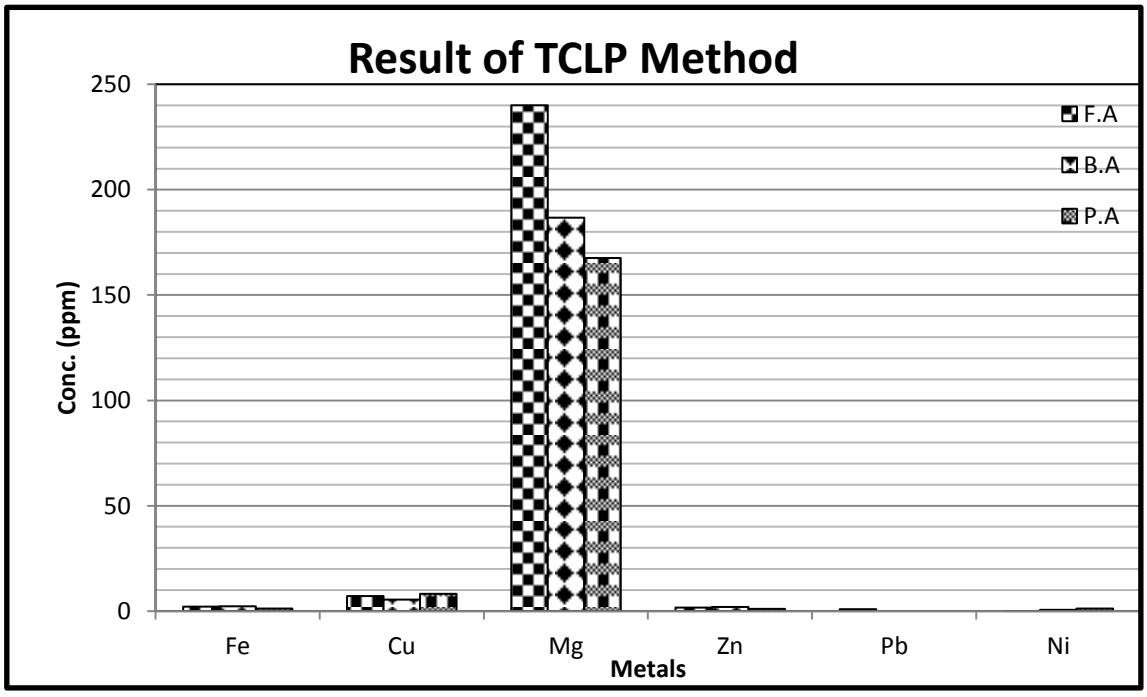

Figure 4.17 Heavy metal concentration of coal ash in TCLP method

The heavy metal concentrations as a result of TCLP are shown in above Table 4.15. In this procedure sodium acetate buffer is used at pH 4.99. Mg and Cu show solubility in

weakly acidic medium and has been leached at higher amounts in all samples. Fe, Zn, Pb & Ni also leached but at very low concentration. Lead is insoluble and does not leach out in TCLP.

The concentration of metals in TCLP is found to be higher than the concentration of metals found in the batch leaching test. This is because metal soluble generally decreases with increase of pH. TCLP involved leaching in slightly acidic buffered condition (i.e. pH = 5) and in the batch leach test, the pH of distilled water to be added is around 7. This is due to precipitation of metal ions as insoluble hydroxides at high pH values.

For all metals, lowest solubility is found in water extract. Trace metal concentration in bottom ash and pond ash are lesser than fly ash. Trace element concentrations are well within the limit of Indian standards for disposal of wastes. A similar comparison of TCLP and batch leaching test indicated that all metals are within specified limits. So the coal ash is used as a dry or wet disposal in the abandoned mine area.

4.11 Mine Water Assessment

Table 4.16 Experimental results of water quality test

Parameter	Sample-1	Sample-2	Sample-3	Permissible limit as per IS 10500:2012
pH	5.01	6.51	7.56	6.5-8.5
Alkalinity (mg/L)	136.7	253	104.7	200-600 mg/L
TSS (Mg/L)	111.3	86.3	94.7	100 mg/L
Turbidity (NTU)	3.8	5.9	2.8	1 - 5 NTU
Hardness (mg/L)	295.7	559.7	426.8	200-600 mg/L
Lead (mg/L)	0	0	0.003	0.01 mg/L
Iron (mg/L)	0.153	0.061	0.014	0.3 mg/L

From Table 4.16 it is found that near the abandoned mine area water is acidic in nature pH = 5.01), which is below the drinking standard and the pH value of water collected away from the mines is increasing (at source 2 it is 6.51 and at source 3 it is 7.56) which is

between the permissible limit of Indian standards. Results of alkalinity of sample-1 and sample-3 are below the acceptable limit of IS standard and sample-2 results in the range of acceptable limits. Total suspended solid (111.3 mg/L) of sample -1 is above the IS standard which is harmful to the environment. Turbidity of the sample – 2 (5.9 NTU) is above the Indian standard range and the other two samples (3.8 & 2.8 NTU) are in the acceptable limit of IS 10500: 2012. Hardness of all 3 samples (295.7, 559.7 and 426.8 mg/L) is in between standard of drinking water (200-600 mg/L). For samples -1 and 2 lead percentages are not found, but from sample–3 percentage of lead is found, it was in permissible liquid. The concentration of iron is found below the acceptable limit.

The water collected from near the abandoned coal mine is acidic in nature (pH =5. 01) and other parameters (turbidity, hardness, alkalinity, TSS, lead and iron) are as per IS 10500:2012.

The water collected from 500 m away from abandoned coal mine is high in turbidity and other parameters are within the IS standard. The water collected from 1 km away from abandoned coal mine is in the range of drinking water standard.

4.12 Coal Ash Slurry and Mine Water Interaction

4.12.1 Coal Ash Slurry

The coal ash slurry has been prepared in 1:10 proportion. The pH of the coal ash is given in Table 4.17.

Table 4.17 pH value of coal ash slurry

Slurry Type	pH Value
Fly Ash	8.83
Bottom Ash	8.94
Pond Ash	8.75

After slurry preparation the pH value of coal ash is increased 7 to 8.3 in 1 hour.

4.12.2 Coal ash slurry- mine water interaction

The Coal ash slurry and mine water mixed with 1:1 proportion and the pH values were given in Table 4.18.

Table 4.18 pH value of coal ash slurry and mine water mix in 1:1

Slurry	After 1hour pH	After 24 hour pH
Fly ash	8.15	6.72
Bottom ash	8.37	6.93
Pond ash	8.25	6.79

When the alkali slurry (i.e. pH = 8.83) mixes with acidic mine water (i.e. pH=5. 01) in 1:1 proportion its pH decreases slightly in 1 hour and after 24 hours it decreases and come to the level of drinking water standards.

Coal ash slurry and mine water mixed with 1:2 proportion and the pH values were given in Table 4.20

Table 4.19 pH value of coal ash slurry and mine water mix in 1:2

Slurry	After 1hour pH	After 24 hour pH
Fly ash	7.84	6.66
Bottom ash	7.90	6.94
Pond ash	7.78	6.71

When the alkaline slurry mixes with acidic mine water in 1:2 proportion its pH it decreases slightly in 1hour as compared to 1:1 mix slurry and after 24 hours it decreases and come to the level of drinking water standards.

CHAPTER-5

CONCLUSION

In the present study, the coal ash sample have been collected from Talcher Super Thermal Power Station (TSTPS), Kaniha and water samples have been collected from Mahanadi coal field, Talcher area. The mineralogical, morphological, chemical and geotechnical characterizations of coal ash have been carried out. The leaching behaviour of coal ash has been studied. The pH, turbidity, alkalinity, total suspended solids, iron and lead content of the collected water samples from the abandoned coal mines have been determined. The changes in slurry mine water interaction are also studied and the following conclusion has been drawn

- Bottom ash absorbs more water and allows less water to the ground due to higher water holding capacity. Water holding capacity is inversely proportional to the particle size of the material.
- Quartz, Mullite and Hematite minerals are greatly available in coal ash.
- The spherical morphology of the pond ash and fly ash creates the ball-bearing effect which affects a frictionless flow in the pipe with low wear and tear. So it can be stated that, the fly ash and pond ash is good for filling in an abandoned mine.
- From the chemical composition of coal ash it is found that it is Class ‘F’ fly ash. As per ASTM – 618 Class ‘F’ fly ash is a better filler material than Class ‘C’ fly ash.
- The TSTPS coal ash is slightly acidic in nature.
- Trace metals concentration in fly ash is more than pond ash and bottom ash in both acidic and alkali medium.
- Water sample collected near the Mahanadi Coal Field abandoned mines is acidic in nature.

- pH value of coal ash as found by mixing distilled water is slightly acidic (i.e. pH=7.21). However, on mixing with normal tap water, it is becoming alkaline (i.e. pH=8.94).
- When the alkali slurry mixes with acidic mine water its pH value decreases slightly in 1hour and after 24 hours it decreases substantially and attains to the pH value (around 6.91) confirming to the drinking water standards.

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